Final report on electron transport and thermal transport simulation using *ab initio* methods

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14. ABSTRACT

In this project, the uniquely-developed TOhoku Mixed Basis Orbital ab initio calculation package (TOMBO) was used in simulations of electron and thermal transport in a small molecule organic-based circuit and in a GeSe supercell, respectively. For the small molecule, application of a bias lead to a non-equilibrium state for which Density Functional Theory (DFT) is not directly applicable. The simulation proved useful by modifying TOMBO by separating the whole system (circuit) into three parts: right and left semi-infinitive leads, and finite organic molecule. Since TOMBO uses two different types of basis sets (plane-waves and atomic orbitals) maximally localized Wannier function (Wannier90) was introduced to realize the separation. Since the two semi-infinitive leads are very close to their equilibrium state, non-equilibrium Green function (NEGF) was used to represent them by self-energy terms. Introduction of bias affected periodic boundary conditions, but were satisfied by introducing a potential drop in the vacuum. Simulation of thermal conductivity versus temperature was considered for a 6x6x6 k-mesh involving a crystalline, orthorhombic GeSe supercell. Its thermal conductivity tensor is diagonal, with three different values along the 3 principal axes. This work examined the third trace of that tensor and the contribution of the different branches. Acoustic branches usually contribute most to the thermal conductivity as their group velocity and lifetimes are largest. In this case, each of the acoustic modes contributes to about 20% of the total value. The first 3 branches contribute to almost half the total thermal conductivity.

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1. First-principles calculation of Electron transport through organic molecule

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Motivation:

The motivation of our study is to realize the organic molecular conductivity computation based on the first-principles calculation. Organic molecules are considered as one of the prospective candidates of the next-generation circuit. As shown in the figure, the molecule connects to the two leads. If the bias is applied, the electron current flows through the molecule. The I-V curve is calculated self-consistently. The computation is realized by self-developed package TOMBO.

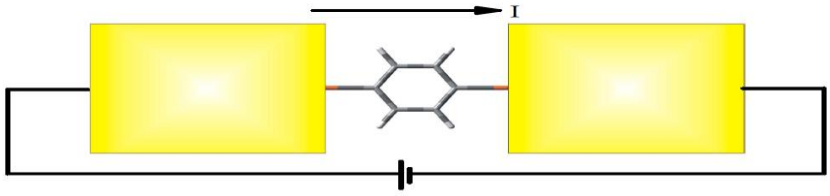

Fig. 1. Benzene is connected with two Au leads

Different from the traditional density functional theory (DFT) method, the present system is divided into two infinitive leads connecting with organic molecules (shown in Fig. 1.). The whole is in non-equilibrium after applying the bias. Therefore, we cannot apply the DFT calculations directly. To achieve the computation by using TOMBO, some modifications are required.

Methods:

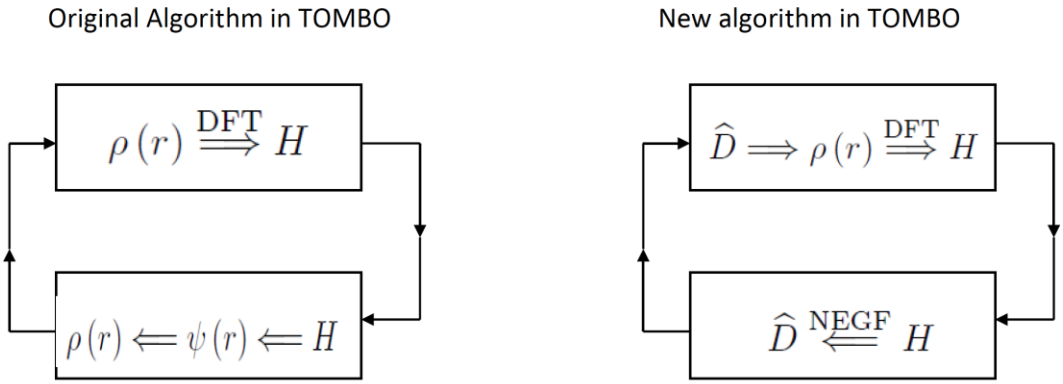

Fig. 2. The algorithms used in traditional DFT calculations and transport calculations.

In traditional DFT calculations, the equations are solved self-consistently (shown in Fig. 2.). Firstly, based on DFT, the initial density distribution results into the Hamiltonian of the system. Then, from statistical mechanics, diagonalization of the Hamiltonian achieves new distribution. Generally speaking, this new

distribution is different from the previous one. Applying the self-consistent process, the system is calculated until the criteria are satisfied.

However, in present case, since the introduction of two semi-infinitive leads, the whole system, which has no periodicity, is infinitive. The traditional DFT fails to deal with the infinitive system. Therefore, non-equilibrium Green function (NEGF) is introduced and two semi-infinitive leads are represented by self-energy terms.
Compared with the traditional DFT process, the first step is same: the Hamiltonian comes from the density distribution. But the second step is replaced, and the new density distribution stems from the NEGF rather than the statistical mechanics.

NEGF:

The Hamiltonian (H) of the system reads,

$$H = \sum_{k,i} \epsilon_{ki} c_{ki}^{\dagger} c_{ki} + \sum_{l} E_l d_l^{\dagger} d_l + \sum_{k,i,l} V_{ki,l} c_{ki}^{\dagger} d_l + c.c$$

The first term is the energy levels of the leads, the second term is the energy levels of the molecules connecting with the leads and the last two term stand for the coupling between the molecules and the leads.
The self-energy term is,

$$\Sigma_i^R = V_{Mi} g_i^R V_{Mi}^{\dagger}$$

where g_i^R is the surface Green function. After achievement of self-energy, we can get the new density matrix,

$$\widehat{D} = -i \int_{-\infty}^{\infty} dE \left[\frac{G^{<}(E)}{2\pi} \right]$$

The density matrix and the Hamiltonian are solved self-consistently, and the current is calculated if the criteria are satisfied.

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \mathrm{Tr}(\Gamma_1 G^R \Gamma_2 G^A)(f_2(E) - f_1(E))$$

where f_i is the Fermi distribution of the ith lead and

$$\Gamma_{1(2)} = i[\sum\nolimits_{1(2)}^{R} - \sum\nolimits_{1(2)}^{A}]$$

which represents the broaden of the energy levels.

Wannier Function:

The basis sets used in TOMBO is mixed basis sets.

$$\Psi^{\lambda}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}}^{\lambda} \frac{e^{i\mathbf{G}\cdot\mathbf{r}}}{\sqrt{\Omega}} + \sum_{j} \sum_{nlm} c_{jnlm}^{\lambda} \Phi_{jnlm}(\mathbf{r} - \mathbf{R_j})$$

In the mixed basis sets, there are two parts. One is plane waves basis sets, the other is atomic basis sets.
The plane waves are non-localized. To divide the whole system into three parts, we have to introduce Wannier function. In our program, we will use maximally localized Wannier function (MLWF).
If Wannier function is achieved, we can express the Hamiltonian operator in real space by using the definition:

$$|Rn\rangle = \frac{V}{(2\pi)^3}\int \sum_{m=1}^{N} U_{mn}^{k} |\psi_{mk}\rangle e^{-ik\bullet R} dk$$

where U^k is the unitary matrix. The strategy consists of choosing the U that minimize the sum of the following spreads of the Wannier functions about their centers:

$$\Omega = \sum_n \left[\langle 0n | r^2 | 0n \rangle - \langle 0n | r | 0n \rangle^2 \right] = \sum_n \left[\langle r^2 \rangle_n - \bar{r}_n^{\,2} \right]$$

The matrix elements of the position operator between Wannier functions may be expressed in reciprocal space as:

$$\langle Rn | r | 0m \rangle = i \frac{V}{(2\pi)^3} \int e^{ik\bullet R} \langle u_{nk} | \nabla_k | u_{mk} \rangle dk$$

$$\langle Rn | r^2 | 0m \rangle = -\frac{V}{(2\pi)^3} \int e^{ik\bullet R} \langle u_{nk} | \nabla_k^2 | u_{mk} \rangle dk$$

If the Wannier function is achieved, we can get the self-energy and calculate the current through the molecule.

Outlook:

Since the periodic boundary condition should be valid in the calculation, the application of the electric field breaks the translation invariance. To recover the periodic boundary condition, the saw-tooth like potential should be applied in our calculation. So far, the application of the electric field is not available in TOMBO, we have to modify the source code and make it possible.

Conclusion:

1) The whole system should be separated into three parts, left semi-infinitive lead, finite organic molecule, and the right semi-infinitive lead. Since two different types of basis sets, namely plane-waves and atomic orbitals, are used in TOMBO, we introduce the maximally localized Wannier function (Wannier90), to realize the separation.

2) The infinitive system cannot be calculated directly. Given the fact that two leads are very close to their equilibrium state, non-equilibrium Green function (NEGF) is used, and two semi-infinitive leads are represented by self-energy terms. These self-energy terms have the same dimensions as

the organic molecule. Therefore, the infinitive system is equivalent to the finite organic molecule plus two finite self-energy terms.

3) In the calculation, the periodical boundary condition should be satisfied. However, if the bias is applied, the potential drop is found in the two leads to counter-balance the applied bias. Unfortunately, this is not the real case. To solve this problem, we introduce the potential drop in the vacuum. Therefore, electrostatic potential of two leads is homogeneous, and the leads can be replaced by two self-energy terms.

1. First-principles calculation of thermal transport in GeSe

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GeSe as a IV-VI chalcogenide material, has good potential as a thermoelectric material. Our goal in this project is to apply our newly-developed methodology[1] to calculate its phonon dispersion and thermal conductivity.

In the previous reports, from the first-principles DFT calculations in a large supercell containing 480 atoms, we obtained the phonon dispersion and showed that a large number of neighbor interactions needs to be included in order to produce the correct phonon dispersion.
Due to the low symmetry of the structure and the nature of the chalcogenide element, the phonon calculations did not converge until the range of interactions were increased up to 8 A^o . This includes up to 41 st nearest neighbors in the harmonic force constants. Cubic FCs were included up to 5th shell and quartic up to the second shell.

Figure 1 shows the decay of harmonic spring constants versus distance when up to 76 neighbor shells, corresponding to a pair distance of 9.42 A^o are included in the fitting. This figure shows that changing the number of included force constants does not change their actually fitted value. Due to the heavy size of the calculations, the k-point summation in the calculation of the phonon lifetimes included a 6x6x6 mesh in the full Brillouin zone. Results presented in this report refer to this mesh. We need however to perform calculations with a larger k-mesh in order to obtain results which are converged with respect to the number of kpoints. Usually an extrapolation procedure[1] needs to be performed in order to reach the converged value.

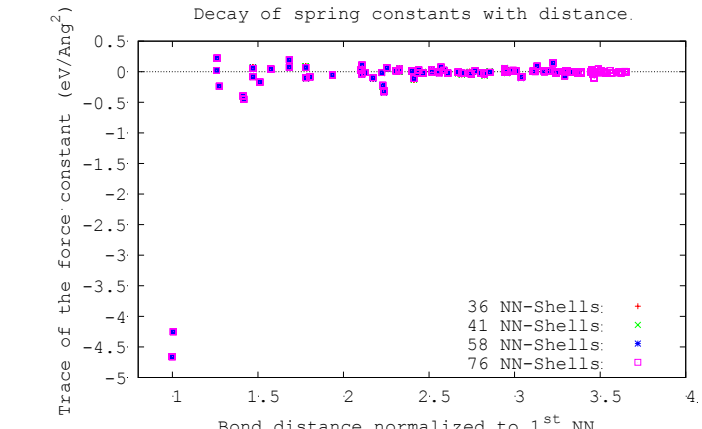

Figure 1: Spring constants versus neighbor distance, normalized to the nearest neighbor which is 2.57 A.

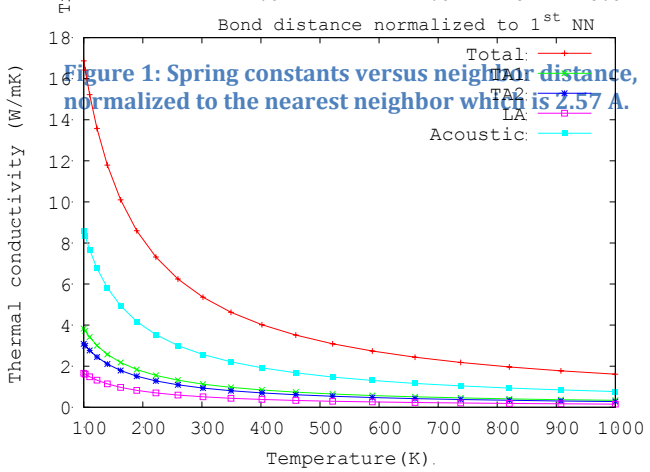

Figure 2: Total and partial thermal conductivity versus temperature. The contribution of the 3 acoustic modes and their sum is being compared to the total thermal conductivity.

Figure 2 shows the thermal conductivity versus temperature with the considered 6x6x6 k-mesh. Given that the crystalline structure of GeSe is orthorhombic, the thermal conductivity tensor is diagonal, with three different values along the 3 principal axes. Here we are reporting the third of the trace of that tensor. The contribution of different branches can also be considered. Usually the acoustic branches contribute most to the thermal conductivity as their group velocity as well as their lifetimes are largest. In this case, each of the acoustic modes contributes to about 20% of the total value. As can be seen from this figure, the first 3 branches contribute to almost half the total thermal conductivity.

In the future, we will examine the convergence of the results with respect to the fineness of the k-mesh chosen in the first Brillouin zone. These are very heavy calculations which scale as the cube of the number of modes (=24 in this case). Large unit cells would require much more computational resources than the more simple primitive cells which contain one or two atoms. Once the convergence is achieved, phonon relaxation times and mean free paths will also be calculated and displayed. Their contribution to the heat transport will accordingly be discussed.

References:

[1] K. Esfarjani, G. Chen and H. T. Stokes, "Heat transport in silicon from first-principles calculations," *Phys. Rev. B* 84, 085204 (2011).